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FROM: PROI (TI) (STINFO)

03 October 2000

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HEDM Contractors Conference (Park City, UT, 24 Oct 2000)
(Deadline: 27 Sep 2000 – PAST DUE)

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THEORY AND SYNTHESIS OF NEW HIGH ENERGY DENSITY MATERIALS

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The aim of this AFOSR program is the synthesis of novel HEDM compounds, exploiting the synergism between theory and synthesis. Theoretical calculations are routinely used to guide the synthesis efforts and to facilitate the identification and characterization of the products.

Under DARPA sponsorship, the synthesis of novel polynitrogen compounds was pursued. Last year, the successful synthesis of $N_5^+AsF_6^-$ had been reported. The N_5^+ cation is only the third known, homoleptic polynitrogen species that can be prepared and isolated in bulk, the other two being N_2 and the azide anion. $N_5^+AsF_6^-$ was only marginally stable and can explode. The N_5^+ cation has now been successfully tamed by preparing the stable fluoroantimonate salts, $N_5^+SbF_6^-$ and $N_5^+Sb_2F_{11}^-$. The former is stable up to 70 °C and, according to drop weight tests, is essentially insensitive. The crystal structure of $N_5^+Sb_2F_{11}^-$ was determined, and the geometry of N_5^+ was found to be in excellent agreement with that predicted by our theoretical calculations. A considerable amount of effort was spent on improving the syntheses of the precursors for N_5^+ salts. This work resulted in the discovery of a new *cis-trans* isomerization process for N_2F_2 and a disproportionation reaction of N_2F_2 to give $NF_4^+Sb_3F_{16}^-$ under mild conditions. Metathetical reactions were carried out between $N_5^+SbF_6^-$ and alkali metal azides in pursuit of N_8 . Furthermore, reactions of $N_2F_3^+$ and N_2F_2 with HN_3 were studied. Attempts were made to find a easily accessible replacement for N_2F^+ in its reactions with HN_3 to give N_5^+ . To this end, the protonation of N_2O was studied with N_2OH^+ being the desired product, but all reactions were unsuccessful.

Efforts to prepare the N_{11}^+ cation by the reaction of $N_2F_3^+$ with 3 moles of HN_3 were unsuccessful. The $N_2F_3^+$ cation was initially reduced by HN_3 to N_2F^+ which then proceeded to react with HN_3 to give N_5^+ .

While carrying out structural studies of the NF_2O^+ cation, which is another potential precursor for polynitrogen compounds, a new method for solving oxygen/fluorine positionally disordered crystal structures was discovered. This method was also successfully demonstrated for the SO_2F^- anion. In both cases, it was shown that the crystal structures obtained from disordered data sets with our method were in excellent agreement with those predicted by the theoretical calculations for the free gaseous ions.

In pursuit of novel powerful oxidizers that might be stronger than any presently known oxidizer, the following new concept was developed and tested. Cations are stronger oxidizers than their neutral parent molecules, which in turn are stronger oxidizers than their anions. Therefore, transition metal fluoride anions were prepared in their highest oxidation states by high temperature / high pressure fluorinations with elemental fluorine and then converted to the corresponding cations by acidification with strong Lewis acids. The resulting, thermally unstable cations are indeed very powerful oxidizers. This was successfully demonstrated for the NiF_3^+ system, which was shown to be capable of oxidizing ClF_3 and BrF_5 to ClF_6^+ and BrF_6^+ , respectively. However, attempts to use this system for the preparation of the new OF_3^+ or XeF_7^+ cations were not successful. In a quest for finding the strongest possible oxidizer, the oxidizing strength of numerous transition metal fluoride cations that can be prepared in this manner, are presently being calculated by ab initio methods in collaboration with Dave Dixon. In connection with this work, the crystal structures of ClF_6^+ , BrF_6^+ , and IF_6^+ were determined in collaboration with McMaster University and their force fields were calculated by ab initio methods.

The study of the ClF_4^+ cation, which was started last year, was completed, and extensive theoretical modeling of the influence of strong intermolecular fluorine bridging on the structure and the vibrational spectra was carried out. A simple method for simulating infinite chains by capping with HF was devised and shown to give excellent results. Results from a theoretical study of the closely related BrF_4^+ and IF_4^+ cations strongly disagreed with the previously

reported crystal structures and prompted their reinvestigation. It was shown that the previously reported structures were indeed in error and that the correct structures are in excellent agreement with the theoretical predictions. In the case of $\text{IF}_4^+\text{SbF}_6^-$ a very interesting 9-coordinated environment was found for IF_4^+ . In collaboration with Arkady Ellern, the crystal structure of solid ClF_3O was also determined and shown to consist of unusual tetrameric units.

Attempts to prepare and characterize the yet unknown PO_2^+ cation, the analogue to the well-known NO_2^+ cation, resulted in a surprise. Acidification of PO_2F_2^- salts with SbF_5 did not produce the expected $\text{PO}_2^+\text{SbF}_6^-$ but a tetrameric ring structure with P-O-Sb bridges and terminal P-F bonds. Similarly, attempts to prepare the novel LiF_2^- anion in the form of its Cs^+ salt gave an unexpected highly bridged crystal structure with the correct composition but tetra-coordinated Li and octa-coordinated Cs.